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## MODERN PHYSICAL CHEMISTRY.

*The Theory of Electrolytic Dissociation.* By H. C. Jones. Pp. xii + 289. (New York: The Macmillan Company. London: Macmillan and Co., Ltd., 1900.)

THE theory of electrolytic dissociation is only some fifteen years old, but in that short time its growth has been very great, and its suggestiveness most marked. We gladly welcome a volume on the subject by one who has himself done much to promote its advance, and to render more secure some of the positions it has taken.

The author's preface explains his object; he has been asked from time to time where an account of the newer developments of physical chemistry is to be found. Original memoirs are not always accessible to a student, and in many cases explanation is wanted, and further development of an argument or line of thought may prove helpful; and so Mr. Jones has given us a book based in the main directly on the work of van 't Hoff, Ostwald, Arrhenius and the others who have made the theory, but in which the numerous developments of Arrhenius' original idea are skilfully brought together, and the bearing of the theory on phenomena, apparently widely diverse, is clearly shown. The plan of the book is in the main a good one. The first chapter is devoted to the earlier physical chemistry with the object of showing its relation to that which was to follow; accounts are given of Kopp's work on the boiling points of liquids and on molecular volumes, of the researches of Lorentz, Gladstone and Dale, Le Bel and van 't Hoff and Perkin on optical properties. The investigations of Favre and Silbermann, Berthelot and Julius Thomsen into thermal chemistry, the electrolytic work of Faraday and Clausius, Hittorf and Kohlrausch, are described; and an interesting and important discussion of the development of chemical dynamics and chemical statics concludes the chapter.

In the explanation of Guldberg and Waages' Law of Mass Action, there is a vague and somewhat unsatisfactory use of the word *force*; we are told that

"if we represent the active masses of two substances by  $m$  and  $n$ , and the coefficient depending on the nature of the substance, &c., by  $c$ , the force of the chemical reaction is expressed by  $mnc$ ."

"Force" has no meaning used in this connection, the mass of compounds, or the number of molecules of compounds produced, can clearly be put equal to  $mnc$ , and the condition of equilibrium will be reached when this mass is equal to the mass of matter combining to form the original substance. There is an obvious misprint on page 62;  $k/h$  is clearly written for  $c/c$  of page 61.

In Chapter ii. we are introduced to the main subject of the book. An account is given of van 't Hoff's original paper "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases" (*Zeitschrift für physikalische Chemie*, i. p. 481), and the grounds for believing that in certain solutions the osmotic pressure conforms exactly to the three gaseous laws of Boyle, Gay Lussac and Avogadro are stated. Attention is here drawn to the large class of compounds, all the acids, all the bases, and all the salts, which form exceptions to the above statement. For these the law is no longer  $PV = RT$ , but

$PV = iRT$ , where  $i$  is a coefficient always greater than unity, to which a meaning is given when we consider the work of Arrhenius.

According to this the molecules in an electrolyte, or some of them, are dissociated into ions. The electrolytic effects depend on the dissociated or active molecules; let these be  $n$  in number, and suppose each is divided into  $k$  parts; suppose also that there are  $m$  molecules remaining inactive or undissociated, then the total number of molecules is  $m + n$ , the number of inactive molecules and ions is  $m + kn$ , and the value of van 't Hoff's coefficient  $i$  is shown to be  $(m + kn)/(m + n)$ .

Arrhenius' theory of electrolysis is an extension of that of Clausius. Clausius had shown that in an electrolyte it was necessary to suppose some molecules of the dissolved salt were broken up into ions; Arrhenius explained how to determine from observations on osmotic pressure the number of such molecules in a given solution.

From this we are led on to two interesting chapters—"Evidence for the Theory" and "Applications of the Theory"; the evidence which the author has accumulated is most valuable, while the fertility and resourcefulness of the theory are strikingly shown. The book will be very useful; at the same time, in one respect, it is open to criticism of some importance. A student not unnaturally asks, What is osmotic pressure due to? Why, under certain circumstances, does liquid run into a closed vessel apparently against the pressure? What is the mechanism by which such a process is managed? It may be answered, We do not know! The author may fairly wish to use language independent of any molecular theory, and not bind himself down in any way; it is enough for many purposes, it may be said, to know that there is a definite pressure in such a solution without inquiring how that pressure is caused. At the same time it is impossible to avoid alluding to molecular impacts and the like; there is no evidence that Mr. Jones does wish to avoid it, and in places, *e.g.* p. 95 and elsewhere, he refers to the modern kinetic theory of gases, and we think—this is the criticism—that it would have made the book clearer if he had based his explanation throughout on the extension of that theory to liquids. When an ordinary experiment for measuring osmotic pressure is started with a solution inside a vessel closed with a semi-permeable membrane, the number of water molecules which strike a unit of area of the interior surface in any given time is less than the number striking the same area on the outside; thus more molecules of water enter the space than leave it; the molecules of the salt cannot pass the membrane, hence the pressure inside increases. The tendency is both for the water and the dissolved substance to distribute themselves uniformly; the pressure inside is due to the impacts (1) of the water, (2) of the dissolved substance that outside arises from the impacts of the water only; ultimately the pressures due to the water balance, and the excess of pressure inside measures the effect due to the impacts of the dissolved substance.

The whole is merely an example of the first proposition of Mr. Jones' third chapter. The physical properties of completely dissociated substances should be additive. This is all implied in the book; it might with advantage be stated more precisely.

Another matter with regard to which a greater definiteness seems desirable, even at the expense of some generality, is the theory of the action of the voltaic cell.

Nernst's theory of the electrolytic "solution-tension" of a solid—solution-pressure is a preferable term—is stated in his own words, but they are vague :

"We must ascribe," it is said, after a reference to osmotic pressure, "to a dissolving substance in contact with a solvent, similarly, a power of expansion, for here also the molecules are driven into a space in which they exist under a certain pressure. It is evident that every substance will pass into solution until the osmotic partial pressure of the molecules in the solution is equal to the 'solution-tension' of the substance" (pp. 231-232).

We may put the whole theory slightly differently, thus :—

In the case when a substance is being dissolved in such a way that *molecules* pass from the solid into the liquid, the pressure rises in consequence of the impacts of these molecules on the walls of the containing vessel ; now when molecules also pass from the liquid into the solid, the "evident" fact is that the steady state is reached when the numbers entering and leaving the liquid are the same. In such a case the osmotic pressure measures the solution-pressure, and no electrical action is involved.

But now let us suppose that a metal is passing, not in the form of *molecules*, but in that of *ions* into water. Each of these ions carries with it a positive charge ; the water therefore tends to become positive, the metal negative, and an electrical double layer is formed over the surface of separation. The charged ions are not free to move throughout the water, but few escape from the surface ; hence the additional pressure due to the impacts of the metallic ions—the solution-pressure, as it is called—is small.

Again, let us take the case of a metal, such as copper, in a solution of one of its own salts, say copper sulphate ; here, also, if there were no electrical effects, we might suppose that copper *molecules* would be deposited out of the sulphate on to the metal, while other molecules would leave the metal ; the steady state would be reached when these two sets of molecules became equal in number, and the osmotic pressure would become—in reality, unless the solution were very weak, would *fall* to—the solution pressure. But according to the theory, the copper passes as *ions* which carry with them out of the solution their positive charge ; this they give up to the metal on becoming molecules. And since we suppose that, unless the solution be very weak, the number of copper ions leaving it is, to start with, greater than those entering, the metal becomes positive, the negative ions of the solution are attracted to it, the positive ions driven off, a double layer is again formed ; a difference of electrical potential is established between the metal and the solution—the metal being positive, the solution negative.

If, however, we consider a metal, such as zinc, which has a high solution pressure when immersed in, say, zinc sulphate, we must suppose that at the start more metallic ions leave the metal than enter it, the solution thus becomes positive, the metal negative, and the double layer formed is one which tends to prevent the positive metallic ions from leaving the zinc, and is thus opposite to that formed on the copper.

In both these cases we must suppose, when the steady state is reached, that the ions leaving the metal leave it under the solution pressure of the metal in the liquid. This may be seen as follows : If there were no electrical force called into action, the pressure would go on changing in the liquid up to the solution pressure, when the number of metallic ions leaving the surface would balance those entering.

Thus the solution pressure measures the whole amount of momentum which the ions of the metal tend to transfer per second across unit area of the surface. Now according to the theory this momentum depends on the metal only, and the tendency to transfer momentum remains the same, however the transfer be stopped ; in reality, the electrical forces acting across the double layer stop it, not the opposing momentum of the liquid ions, and the pressure exerted by these electrical forces must be therefore equal to the solution pressure of the solid, *i.e.* when a current is flowing the positive ions start from the metal at the solution pressure of the metal, and become, when in the solution, ions at the osmotic pressure of the liquid.

Now, however, let us suppose that a piece of copper is connected to the zinc, the two being dipped into zinc sulphate ; and suppose further, for simplicity, that there is no action at the interfaces zinc-copper or copper-liquid, then negative electricity from the zinc passes over to the copper through the zinc-copper junction, attracting to itself the positive ions in the solution and destroying the double layer at the zinc-liquid junction ; thus a current of positive electricity passes through the solution from zinc to copper. The source of the E.M.F. is at the zinc-liquid junction, arising from the fact that more zinc ions pass from the zinc into the solution than from the solution into the zinc ; or, as Nernst would put it, that the solution pressure of the zinc is greater than the osmotic pressure of the liquid. In reality, of course, there may be actions at both the other junctions similar in character to that which we have supposed to go on at the junction of the zinc and the liquid, and the resultant E.M.F. depends on all of these.<sup>1</sup>

In this simple case the energy of the cell is obtained from the passing of the zinc ions from the saturation pressure of the zinc to the osmotic pressure of the liquid, and we obtain at once Nernst's expression for the electromotive force, varying as  $RT \log_e P/p$ , where  $P$  is the saturation pressure,  $p$  the osmotic pressure.

But an article which started as a notice of Mr. Jones' most useful book is in danger of becoming a dissertation on the seat of the electromotive force of a voltaic cell, a result to be avoided.

R. T. G.

#### MESOZOA AND ENANTIOZOA.

*Traité de Zoologie Concrète*. T. ii. 1<sup>re</sup> partie. *Mésozoaires—Spongiaires*. By Yves Delage and Edgard Hérouard. Pp. ix + 244. (Paris : C. Reinwald, 1899.)

AS might have been anticipated, this part of the massive "Traité de Zoologie," which is now in course of publication, contains matter of exceptional interest. One-fifth of the present issue is devoted to the Mesozoa,

<sup>1</sup> A reference should be made to Prof. Lodge's article in the May number of the *Philosophical Magazine*, which has appeared since the above was written.